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Thermochemically Consistent Free Energies of Hydration for Di- and Trivalent Metal Ions

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Abstract

This paper uses the relationship between the standard half reduction potential, the third ionization potential, and the free energies of hydration (ΔG_{hyd}) of M^{2+} and M^{3+} ions to calculate new values of ΔG_{hyd} for M^{2+} and M^{3+} ions. The numbers are "thermochemically consistent", i.e. all numbers agree with the applied thermochemical cycle. This enables the tabulation of many ΔG_{hyd} derived mainly from the data compiled by Marcus, but consistent with $\Delta G_{hyd}(H^{+}) = 1100$ kJ/mol and SHE = 4.44 V. The accuracy of the new values of $\Delta G_{hyd}(M^{3+})$ is by definition similar to the accuracy of the experimental hydration energy of the $\Delta G_{hyd}(M^{2+})$ used for calculation, and *vice versa*, i.e. the new data have the same accuracy or higher than previously reported. As a result, the literature values for Cr^{3+} and Au^{3+}, and Pd^{2+} are substantially revised. The approach also allows the calculation of new ΔG_{hyd} for metal ions such as Mn^{3+}, Ti^{2+}, Ag^{3+}, Ni^{3+}, Cu^{3+}, Au^{2+}, and the theoretically interesting but experimentally inaccessible +2 ions of lanthanides. The new numbers enable a discussion of the previously unreported trend in $\Delta G_{hyd}(M^{3+})$ for the 3d metal ions, which relates to the ligand field stabilization energies and effective nuclear charge as for the M^{2+} ions. The new tabulated values should be accurate with the applied assumptions to within 10 kJ/mol and may be of value for other thermochemical calculations, for interpretation of the aqueous trend chemistry of the metal ions, and as benchmarks for theoretical chemistry.

INTRODUCTION

The hydrated metal ions play a central role in living systems and chemistry[1], including many fields of catalysis[2] and in diseases such as Alzheimer's disease[3]. The hydration free energy $\Delta G_{hyd}(M^{n+})$ greatly contributes to the chemistry of the metal ion in aqueous solution[2,4]. For example, $\Delta G_{hyd}(M^{n+})$ is the price paid when transferring a metal ion such as Ca^{2+} to a protein channel in a membrane, or into a protein from solution. The difference in $\Delta G_{hyd}(M^{n+})$ of two metal ions such as Ca^{2+} and Mg^{2+} or Cd^{2+} contributes substantially to the selectivity in their association as host-guest complexes. The $\Delta G_{hyd}(M^{n+})$ also contributes to the dynamic behavior of the metal ion in aqueous solution, its solubility, its tendency to form stabilizing interactions with macromolecules, and its effect on the structure of water itself[1,5].

Experimental values of ΔG_{hyd} also serve as important benchmark data for calculation of other properties, and for the evaluation of theoretical methods such as density functional theory (DFT) and classical force fields[6,7]. When theoretically studying metal ions it is of central importance that ΔG_{hyd} of the charged species is consistently described, as errors in ΔG_{hyd} translate into errors in its computed ensemble-averaged behavior, such as spurious formation of salt bridges or overestimated ion-water interactions; the transport of the ion through water studied by molecular dynamics also depends on the modeled tendency of the ion to stick in its current hydration shell depending on the magnitude of ΔG_{hyd}[8,9].

Most values of ΔG_{hyd} have been tabulated by Marcus[10,11] using the tetraphenylarsonium tetraphenylborate (TATB) extra-thermodynamic assumption required to separate anion and cation hydration terms[12]. Many data have also been tabulated by other prominent researchers such as Noyes[13], Rosseinsky[14], Fawcett[15], and Latimer[16,17]. Since the data by Marcus are the most abundant, they have been used in this work for deriving new free energies of hydration, but other data have also been considered in cases of disagreement, such as for Cr^{3+} (see below). Trasatti has explained in detail how to derive ΔG_{hyd} from the associated standard half potentials $E_{½}^{0}$ and ionization potentials (IP)[18,19]. The reverse transformation includes attempts to identify "absolute" half potentials based on the associated free energies of the thermochemical cycle[18–20]. Of major importance in this context are i) the adherence to consistent standard states (298.15 K; unity activity; 1 atm partial pressure); ii) the use of adequate values of $\Delta G_{hyd}(H^+)$ including consideration of the surface potential of water χ^S, with the consensus $\Delta G_{hyd}(H^+) = -1100 \pm 3$ kJ/mol[21,22]; and iii) the applied convention for the potential of the standard hydrogen electrode (SHE) of $E^0_{SHE}(abs) = +4.44\ V \pm 0.02\ V$[19].

In this paper, thermochemical cycles using the IP, $E_{½}^{0}$, and ΔG_{hyd} have been used to derive new values of ΔG_{hyd} that are all consistent with the $E^{0}_{SHE}(abs) = +4.44$ V and the hydration free energy of the proton $\Delta G_{hyd}(H^{+}) = -1100$ kJ/mol. In addition, the thermochemical cycle enables accurate estimation (± 10 kJ/mol) of many ΔG_{hyd} values not previously reported. Since all values are derived from experimental data only, the new numbers have the same accuracy as the experiments used to evaluate ΔG_{hyd} of the metal ion of the alternative oxidation state, or in some cases better, as explained in individual cases. Notably, the new ΔG_{hyd} values for the 3d M^{3+} ions enable the first analysis of the trend across the 3d transition series in $\Delta G_{hyd}(M^{3+})$ which should be of considerable chemical interest.

METHODS

Conventions used. The thermochemical cycle relevant to the problem can be written as in **Figure 1**. The calculated values refer to the standard states applied in the experimental data from which they were derived, which include unity activities (~1 M concentrations), T = 298.15 K, and 1 atm pressure. The gray color covers the three micro-processes involved in the experimentally determined operational reduction potential, which includes the chemical potential of the electron in the electrode M, the surface potential of water χ^{S}, and the hydration free energy of H_2, $\Delta G_{hyd}(H_2)$, which, as discussed below, is of the order of ~2 kJ/mol. All these terms are components of the experimentally observable standard potential, $E^{0}_{SHE}(abs) = -\Delta G_{el}(SHE)/zF$, where F is the Faraday constant and z is the transferred charge.

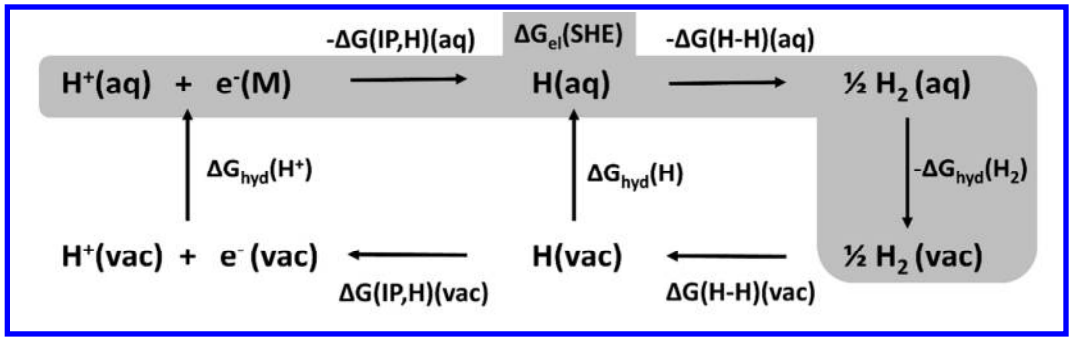

Figure 1. Thermochemical cycle for calculating the absolute potential of the standard hydrogen electrode. The experimentally measured electrode potential $\Delta G_{el}(SHE)$ consists of the processes marked in gray color and includes the surface potential of the solvent (water), χ^{S}.

As discussed notably by Trasatti[19], one can compute E^0_{SHE}(abs) (and thus ΔG_{el}(SHE)) from the three processes of the bottom left of **Figure 1**. The two vacuum terms ½ΔG(H-H)(vac) and ΔG(IP,H)(vac) are accurately known; they represent the free energy of atomization of H_2 and ionization of H in vacuum. ΔG(H-H)(vac) is the bond dissociation free energy of H_2 and equals 406 kJ/mol; it consists of D_0 (H-H) = 436 kJ/mol − 30 kJ/mol TΔS at 298.15 K as given directly by tabulated formation free energies and enthalpies. ΔG(IP,H)(vac) is equal is to the ionization potential of hydrogen (1312 kJ/mol) plus a small 1.8 kJ/mol of TΔS as estimated from the Sackur-Tetrode equation[23]. The remaining free energy, $\Delta G_{hyd}(H^+)$, is the hydration free energy of the proton. As can be seen from **Figure 1**, it involves a phase change from air to water and thus includes χ^S. Most discrepancy between values used in the literature relate to this term, which consequently also affects calculation of ΔG_{el}(SHE)[24].

A long list of $\Delta G_{hyd}(H^+)$ reported by different authors was compiled by Rosseinsky, showing well the heterogeneity in these early numbers[14]; they tend to converge on -1090 ± 5 kJ/mol kJ/mol. The modern consensus value of $\Delta G_{hyd}(H^+)$ is probably −1100 ± 5 kJ/mol: Zhan and Dixon reported -1098 kJ/mol[25] whereas Tissandier et al. reported −1104.5 kJ/mol[21]. These values importantly do not include the surface potential χ^S as they result from interpolation of quantum chemical cluster calculations. Most of the ~10 kJ/mol difference in the values near −1090 kJ/mol and −1100 kJ/mol is thus due to χ^S. The latter are the chemical free energies of hydration whereas the former represent the chemical potential of the proton once it is in water. The standard chemical potential of the proton in water was calculated by Trasatti[19] and Farrell and McTigue[26] to be −1088 kJ/mol. Fawcett[24] derived the value −1088 kJ/mol from the work function of mercury, and another value of −1091 kJ/mol by reassessment of the data of Randles[27]. Thus this number has an accuracy of ± 3 kJ/mol.

If one uses −1100 kJ/mol directly with the thermochemical cycle and the above stated numbers, one obtains ΔG_{el}(SHE) = −4.32 V. This value corresponds to a SHE potential whose value was determined without the surface potential of water. The surface potential was estimated by Trasatti to be +0.13 V[19], by Farrell and McTigue to be +0.025 V[26], and by Krishtalik to be +0.14 V[28]. Parfenyuk estimated a consensus value of +0.10 V from a survey of data[29], which agrees well with the ~10 kJ/mol discussed above. The consensus positive value of the surface potential is physically meaningful and probably accurate to within 0.05 V. The positive value implies that water oxygen atoms tend to be overrepresented at the surface in order to maximize the water-water hydrogen bond interactions; this produces a potential at the surface due to the non-random alignment of dipoles. The present work uses

the +0.13 V by Trasatti as it is close to the density of consensus values and was calculated directly from the chemical potential of the proton. The uncertainty in this number makes the total uncertainty of the calculated values of the order of 0.05 V. Including the +0.13 V produces the commonly defined absolute electrode potential of 4.45 V (note that −1089 kJ/mol is the value of $\Delta G_{hyd}(H^+)$ that gives *exactly* 4.44 V). These points are discussed in detail by Farrell and McTigue, who computed the numbers as 4.31 V and 4.44 V[26]. Each scale has an estimated error of ±0.05 V associated with the thermochemical cycle calculations dominated by the uncetrainty in the surface potential, which translates into 5 kJ/mol for the tabulated values of $\Delta G_{hyd}(M^{n+})$ below. To this uncertainty, one should add the experimental uncertainty in the actual measurement of one value of $\Delta G_{hyd}(M^{n+})$, which is probably largest for the trivalent ions, assuming that errors scale monotonously with the magnitude of ΔG_{hyd}. An estimate of the overall error in the tabulated values is thus ±10 kJ/mol.

Now we discuss the metal ion potentials of interest to the present work. Using a Born-Haber cycle one can calculate the standard half potential for a metal of any given charge, i.e. the process

$$M^{n+} + n\ e^- \rightarrow M \quad (1)$$

as[19]:

$$E_{½}^{0}(M^{n+}/M) = (\Delta G_{at}^{0} + \Delta G(IP_n,M) + \Delta G_{hyd}(M^{n+}))/nF \quad (2)$$

where ΔG_{at}^{0} is the standard atomization free energy of the metal and $\Delta G(IP_n,M)$ is the sum of ionization free energies required to bring M to M^{n+} (i.e. if $n = 2$, it is the sum of the first and second ionization free energies).

The definition of the hydration free energy $\Delta G_{hyd}(M^{n+})$ again depends on whether one includes the surface potential or not. However, when interested in the standard half potentials $E_{½}^{0}(M^{3+}/M^{2+})$, we may write:

$$E_{½}^{0}(M^{3+}/M^{2+}) = E_{½}^{0}(M^{3+}/M) - E_{½}^{0}(M^{2+}/M)$$

$$= (\Delta G(IP_{32},M) + \Delta G_{hyd}(M^{3+}) - \Delta G_{hyd}(M^{2+}))/nF \quad (3)$$

Here, $\Delta G(IP_{32},M)$ is the third ionization potential of M, which is available at very high accuracy in the NIST database. In other words, when calculating the standard half potential between two ions, the atomization free energy and the surface potential cancel out to leave a simple cycle that is calculated with the same accuracy as the accuracy of the *difference* in the experimental hydration free energies, which is similar to or smaller than the accuracy of the experimental $\Delta G_{hyd}(M^{3+})$, which is by far the

largest of the two numbers. When using the thermochemical cycle in **Figure 1**, the SHE = +4.44 V should be used because the standard half potentials refer to this value of SHE, which includes the surface potential.

To summarize the above, this work considers processes involving the $E_{½}^{0}$ of the M^{3+}/M^{2+} redox pairs and uses the consensus values $E^{0}_{SHE}(abs) = 4.44$ V and $\Delta G_{hyd}(H^{+}) = -1100$ kJ/mol. Values of $E_{½}^{0}$ were taken from the electrochemical series reported in the CRC Handbook[30], and from Bratsch for $E_{½}^{0}(Ni^{3+}/Ni^{2+}) = +2.3$ V[31] (data shown in Supporting Information, **Table S1**). The ΔG_{hyd} were derived from the values tabulated by Marcus[10,11]. These assume the TATB approximation and $\Delta G_{hyd}(H^{+})$ of −1056 kJ/mol, and have thus been corrected to the new consensus value of $\Delta G_{hyd}(H^{+}) = -1100$ kJ/mol before use in the cycle. As explained above, one can convert between the thermochemical and operational electrode potentials by using 4.31 V instead of 4.44 V; this is done by making the tabulated ΔG_{hyd} values below 13 kJ/mol smaller. Several other choices can be made for $\Delta G_{hyd}(H^{+})$ and can easily be used to calculate revised ΔG_{hyd} from the data presented here. Notably, if the interest is in conventional free energies of hydration ($\Delta G_{hyd}(H^{+}) = 0$), the value −1100 *n* kJ/mol should be subtracted from the tabulated data in **Tables 1** and **2**.

Note on the hydration free energy of H_2. A small note on the involvement of the hydration of H_2 during measurement of the operational potential: The hydration free energy of H_2 is probably of the order of 2 kJ/mol, which corresponds to an effect on SHE of 0.01 V, and thus this process has little effect even when computing "absolute" potentials. This free energy should resemble the cavitation free energy of water[32] for a cavity with a size of perhaps 3 Å from the center of mass of H_2 to nearest oxygen neighbors[33], or a thermal radius of the cavity of ~2 Å[34]. However, this term does not affect the standard half potentials computed according to Equation (3), and thus does not affect this work's results.

Note on Brønsted acidity of M^{3+}(aq). The thermochemical cycle may involve deprotonation of a water associated with the first coordination shell of the M^{3+} ions, but not the M^{2+} ions, due to the Brønsted acidity of the aqua complexes of the M^{3+} ions. Because the thermochemical cycle is based on the species in solution that give rise to the potential and hydration free energy of M^{3+}, this does not affect the accuracy of the tabulated data but it means that the data refer to the real species during measurement, and not necessarily to the same hydrated state of the M^{2+} and M^{3+} ions. For example, Co^{3+} is well-known to be unstable and is reduced to Co^{2+} unless in very strong acid, and one can

therefore discuss whether the tabulated potentials and hydration free energies of such cases reflect a single species in solution or not.

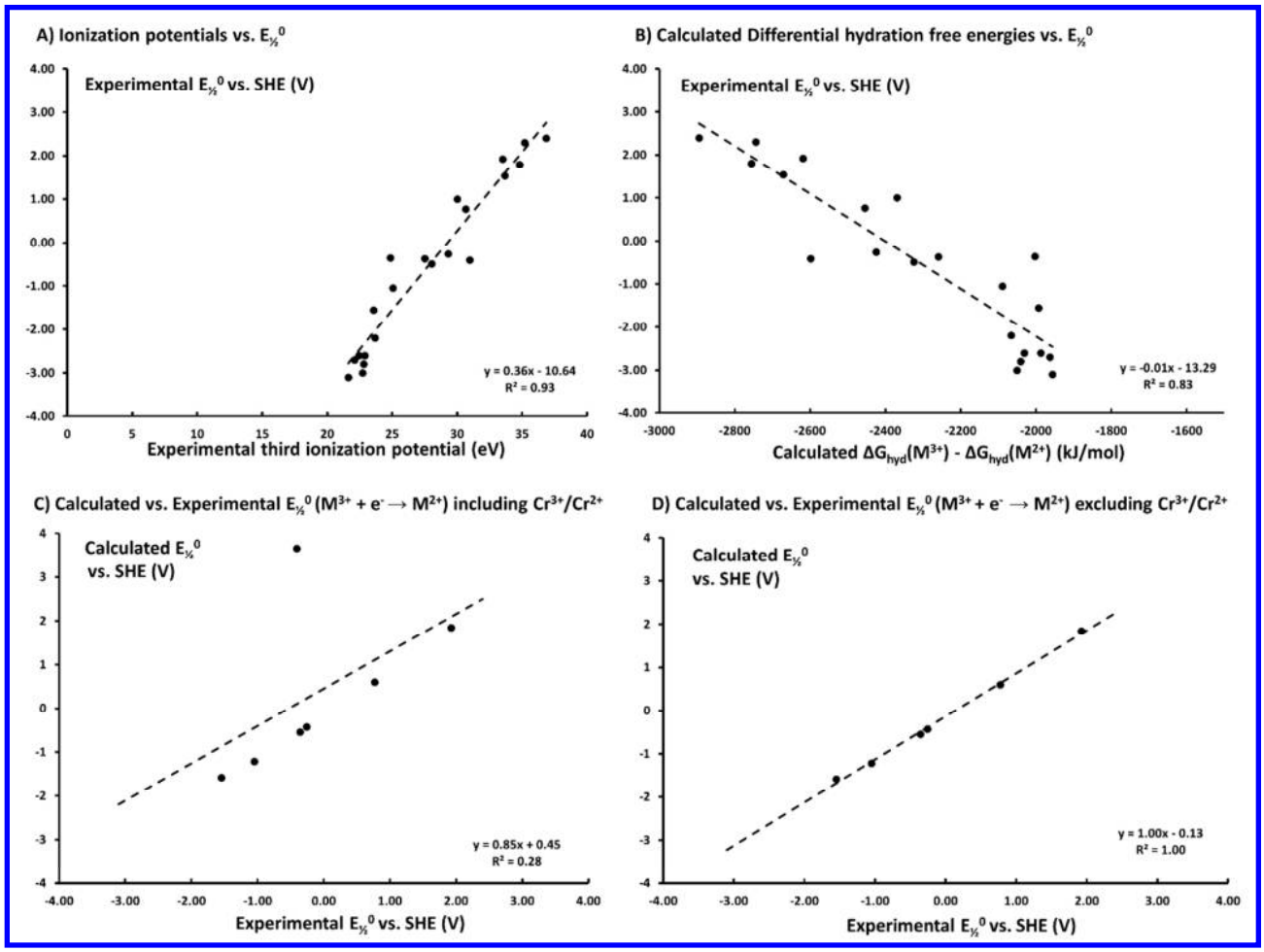

Figure 2. A) Third ionization potential plotted vs. standard half potentials. **B)** The difference in calculated hydration free energies of trivalent and divalent metal ions plotted against standard half potentials. **C)** Experimental vs. calculated standard half potentials using the corrected Marcus data for hydration free energies. **D)** Same as C, but excluding the Cr^{3+}/Cr^{2+} potential (MAD = 0.11 V).

RESULTS AND DISCUSSION

Figure 2A shows the experimental third IP of the metals vs. the experimental $E_{½}^{0}(M^{3+}/M^{2+})$. The correlation is very strong ($R^2 = 0.93$), showing that vacuum IPs largely explain the magnitude of the half potentials in solution, but not perfectly; the scatter is caused by the neglect of the difference $\Delta G_{hyd}(M^{3+}) - \Delta G_{hyd}(M^{2+})$, which varies for the redox couples. **Figure 2B** correspondingly shows the relationship between this difference $\Delta G_{hyd}(M^{3+}) - \Delta G_{hyd}(M^{2+})$ and the experimental $E_{½}^{0}(M^{3+}/M^{2+})$. Also for this property, the correlation is strong ($R^2 = 0.83$). One can conclude from this decomposition in **Figure 2A** and **2B** that both the differential hydration free energy of the redox couple and the vacuum IP contribute approximately similarly to the overall observed standard half potentials, with slightly more importance given to the IPs.

Figure 2C and **Figure 2D** show the relationship between experimental $E_{½}^{0}$ and those computed from the thermochemical cycle using the values by Marcus corrected by (1100-1056)*n* kJ/mol where data are available for both $\Delta G_{hyd}(M^{3+})$ and $\Delta G_{hyd}(M^{2+})$ (Co, Cr, Eu, Fe, Sm, V, Yb). Except for Cr^{3+}/Cr^{2+}, the thermochemical cycle calculations very accurately reproduce the experimental $E_{½}^{0}$ ($R^2 = 1.00$, mean average deviation (MAD) = 0.11 V). The correlation coefficient shows that the thermochemical cycle is complete and sufficient for the purpose of calculation, and is thus used below. The MAD between experimental and calculated half potentials further confirm that the applied procedure has an accuracy of ~10 kJ/mol.

From **Figure 2C** and **Figure 2D** one can conclude that the tabulated ΔG_{hyd} for Cr^{3+} or Cr^{2+} or both is wrong. As shown below, the source of the error in Cr^{3+}/Cr^{2+} half potential originates from $\Delta G_{hyd}(Cr^{3+}) = -4010$ kJ/mol as reported by Marcus, which is too small. For comparison, Gomer and Tryson reported −4367 kJ/mol[20], and Noyes reported −4339 kJ/mol[13]. Using the thermochemical cycle and the corrected value of $\Delta G_{hyd}(Cr^{2+})$ of −1938 kJ/mol, a new value of $\Delta G_{hyd}(Cr^{3+}) = -4536$ kJ/mol is obtained (**Table 1**). This value is essentially the same as that reported by Fawcett[15], −4531 kJ/mol, once the conventional value has been converted for comparison by $\Delta G_{hyd}(H^{+}) = -1100$ kJ/mol.

Table 1. Free Energies of Hydration for Trivalent Metal Ions (kJ/mol).

$\Delta G_{hyd}(H^+)$ = -1100 kJ/mol and SHE = 4.44 V.[a]

	Marcus[10,11]	Marcus, corrected	Noyes[13]	Fawcett[15,b]	This work	Notes
Ag^{3+}	N/A	N/A	N/A	N/A	**-4683**	from E_{32} and $\Delta G_{hyd}(M^{2+}$, this work)
Al^{3+}	-4525	-4663	N/A	-4662	-4657	Marcus corrected value
Au^{3+}	-4420	-4558	N/A	N/A	**-4324**	from E_{32} and $\Delta G_{hyd}(M^{2+}$, this work)
Bi^{3+}	-3480	-3618	N/A	N/A	-3612	Marcus corrected value
Ce^{3+}	-3200	-3338	N/A	N/A	-3332	Marcus corrected value
Co^{3+}	-4495	-4633	N/A	N/A	**-4622**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Cr^{3+}	-4010	-4148	-4339	-4531	**-4536**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Cu^{3+}	N/A	N/A	N/A	N/A	**-4979**	from E_{32} and $\Delta G_{hyd}(M^{2+}$, this work)
Dy^{3+}	-3425	-3563	N/A	N/A	-3557	Marcus corrected value
Er^{3+}	-3495	-3633	N/A	N/A	-3627	Marcus corrected value
Eu^{3+}	-3360	-3498	-3527	N/A	**-3476**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Fe^{3+}	-4265	-4403	-4335	-4416	**-4383**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Ho^{3+}	-3470	-3608	N/A	N/A	-3602	Marcus corrected value
In^{3+}	-3980	-4118	-4100	-4121	-4112	Marcus corrected value
La^{3+}	-3145	-3283	N/A	N/A	-3277	Marcus corrected value
Mn^{3+}	N/A	N/A	N/A	N/A	**-4520**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Nd^{3+}	-3280	-3418	N/A	N/A	-3412	Marcus corrected value
Ni^{3+}	N/A	N/A	N/A	N/A	**-4813**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Pm^{3+}	-3250	-3388	N/A	N/A	-3382	Marcus corrected value
Pr^{3+}	-3245	-3383	N/A	N/A	-3377	Marcus corrected value
Pu^{3+}	-3235	-3373	N/A	N/A	-3367	Marcus corrected value
Sc^{3+}	-3795	-3933	N/A	-3933	-3927	Marcus corrected value
Sm^{3+}	-3325	-3463	N/A	N/A	**-3456**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Ti^{3+}	-4015	-4153	-4046	N/A	-4147	Marcus corrected value
Tm^{3+}	-3515	-3653	N/A	N/A	-3647	Marcus corrected value
U^{3+}	-3205	-3343	N/A	N/A	-3337	Marcus corrected value
V^{3+}	-4220	-4358	N/A	N/A	**-4338**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)
Yb^{3+}	-3570	-3708	N/A	N/A	**-3688**	from E_{32} and ΔG_{hyd} (M^{2+}, Marcus, corrected)

[a] Numbers where previous data are unavailable in the compilations by Noyes, Marcus, and Fawcett are marked bold and underlined; numbers changed by more than 20 kJ/mol are marked in bold. [b] Values reported by Fawcett were converted from conventional data using $\Delta G_{hyd}(H^+)$ = -1100 kJ/mol.

Table 2. Free Energies of Hydration for Divalent Metal Ions (kJ/mol).

$\Delta G_{hyd}(H^+)$ = -1100 kJ/mol and SHE = 4.44 V.[a]

	Marcus[10,11]	Marcus, corrected	Noyes[13]	Fawcett[15,b]	This work	Notes
Ag^{2+}	-1865	-1953	N/A	N/A	-1953	Marcus corrected value
Au^{2+}	N/A	N/A	N/A	N/A	**-1954**	from E_{21} and ΔG_{hyd} (M^+, Noyes)
Ba^{2+}	-1250	-1338	-1314	-1343	-1338	Marcus corrected value
Be^{2+}	-2395	-2483	-2436	-2489	-2483	Marcus corrected value
Ca^{2+}	-1505	-1593	-1588	-1599	-1593	Marcus corrected value
Cd^{2+}	-1755	-1843	-1795	-1820	-1843	Marcus corrected value
Co^{2+}	-1915	-2003	N/A	-2008	-2003	Marcus corrected value
Cr^{2+}	-1850	-1938	-2013	-1924	-1938	Marcus corrected value
Cu^{2+}	-2010	-2098	N/A	-2100	**-2086**	from E_{21} and ΔG_{hyd}(M^+, Marcus, corrected)
Dy^{2+}	N/A	N/A	N/A	N/A	**-1526**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Er^{2+}	N/A	N/A	N/A	N/A	**-1576**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Eu^{2+}	-1385	-1473	N/A	N/A	-1473	Marcus corrected value
Fe^{2+}	-1840	-1928	-1890	-1949	-1928	Marcus corrected value
Hg^{2+}	-1760	-1848	-1820	-1850	-1848	Marcus corrected value
Ho^{2+}	N/A	N/A	N/A	N/A	**-1561**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
In^{2+}	N/A	N/A	N/A	N/A	**-1787**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Mg^{2+}	-1830	-1918	-1900	-1922	-1918	Marcus corrected value
Mn^{2+}	-1760	-1848	N/A	-1859	-1848	Marcus corrected value
Nd^{2+}	N/A	N/A	N/A	N/A	**-1448**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Ni^{2+}	-1980	-2068	-2062	-2087	-2068	Marcus corrected value
Pb^{2+}	-1425	-1513	-1492	-1518	-1513	Marcus corrected value
Pd^{2+}	-1910	-1998	-2397	N/A	-1998	Marcus corrected value
Pm^{2+}	N/A	N/A	N/A	N/A	**-1394**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Pr^{2+}	N/A	N/A	N/A	N/A	**-1420**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Pt^{2+}	-1960	-2048	N/A	N/A	-2048	Marcus corrected value
Ra^{2+}	-1250	-1338	-1280	N/A	-1338	Marcus corrected value
Sm^{2+}	-1375	-1463	N/A	N/A	-1463	Marcus corrected value
Sn^{2+}	-1490	-1578	-1554	-1581	-1578	Marcus corrected value
Sr^{2+}	-1380	-1468	-1421	-1470	-1468	Marcus corrected value
Ti^{2+}	N/A	N/A	-1782	N/A	**-1887**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
Tm^{2+}	N/A	N/A	N/A	N/A	**-1580**	from E_{32} and ΔG_{hyd}(M^{3+}, Marcus, corrected)
V^{2+}	-1825	-1913	N/A	N/A	-1913	Marcus corrected value
Yb^{2+}	-1510	-1598	N/A	N/A	-1598	Marcus corrected value
Zn^{2+}	-1955	-2043	-2022	-2048	-2043	Marcus corrected value

[a] Numbers where previous data are unavailable in the compilations by Noyes, Marcus, and Fawcett are marked bold and underlined; numbers changed by more than 20 kJ/mol are marked in bold. [b] Values reported by Fawcett were converted from conventional data using $\Delta G_{hyd}(H^+)$ = -1100 kJ/mol.

Table 1 and **Table 2** show the new values of ΔG_{hyd} together with those of Marcus, Noyes, and Fawcett, where available, for comparison. Values marked bold differ substantially from previously reported numbers, and values marked bold and underlined are new. The notes to the right describe how the values were obtained, either by correcting the Marcus values or by using the thermochemical cycle of Equation (2). Of particular interest are the new values for 3d M^{3+} ions, discussed further below. It should be noted that the conventional values tabulated by Fawcett generally resemble the values by Marcus, and thus they are generally similar to the values obtained in the present work after correcting to the new consensus $\Delta G_{hyd}(H^+) = -1100$ kJ/mol.

Figure 3 compares the new values of ΔG_{hyd} with those previously tabulated by Marcus and Noyes where data from the latter two authors are available (as mentioned, the data tabulated by Fawcett generally resemble those by Marcus shifted by a few kJ/mol). **Figure 3A** and **3B** compare ΔG_{hyd} for M^{3+} ions from this work with those reported by Noyes and Marcus, respectively. **Figure 3D** and **3E** compare ΔG_{hyd} for M^{2+} ions from this work with those reported by Marcus and Noyes, respectively. The agreement is generally good; however for M^{3+} ions, Au^{3+} and Cr^{3+} values calculated from the thermochemical cycle differ substantially from the values reported previously by Marcus[10,11]. Similarly, the tabulated $\Delta G_{hyd}(Pd^{2+})$ by Noyes (−2397 kJ/mol) also differs substantially from the value obtained in this work after correcting the value by Marcus (−1998 kJ/mol). Below, it argued based on trend comparisons that the new values reported in this work are accurate. When the three conflicting data points for Pd^{2+}, Au^{3+}, and Cr^{3+} are removed, $R^2 = 0.99-1.00$ for the comparison of data from this work and those compiled by Marcus and Noyes (**Figure 3C** and **Figure 3F**). The agreement confirms the expectation that the new data derived in this work (marked bold in **Table 1** and **Table 2**), which were not previously reported by Noyes, Fawcett or Marcus, should have a similar accuracy as the experimental numbers.

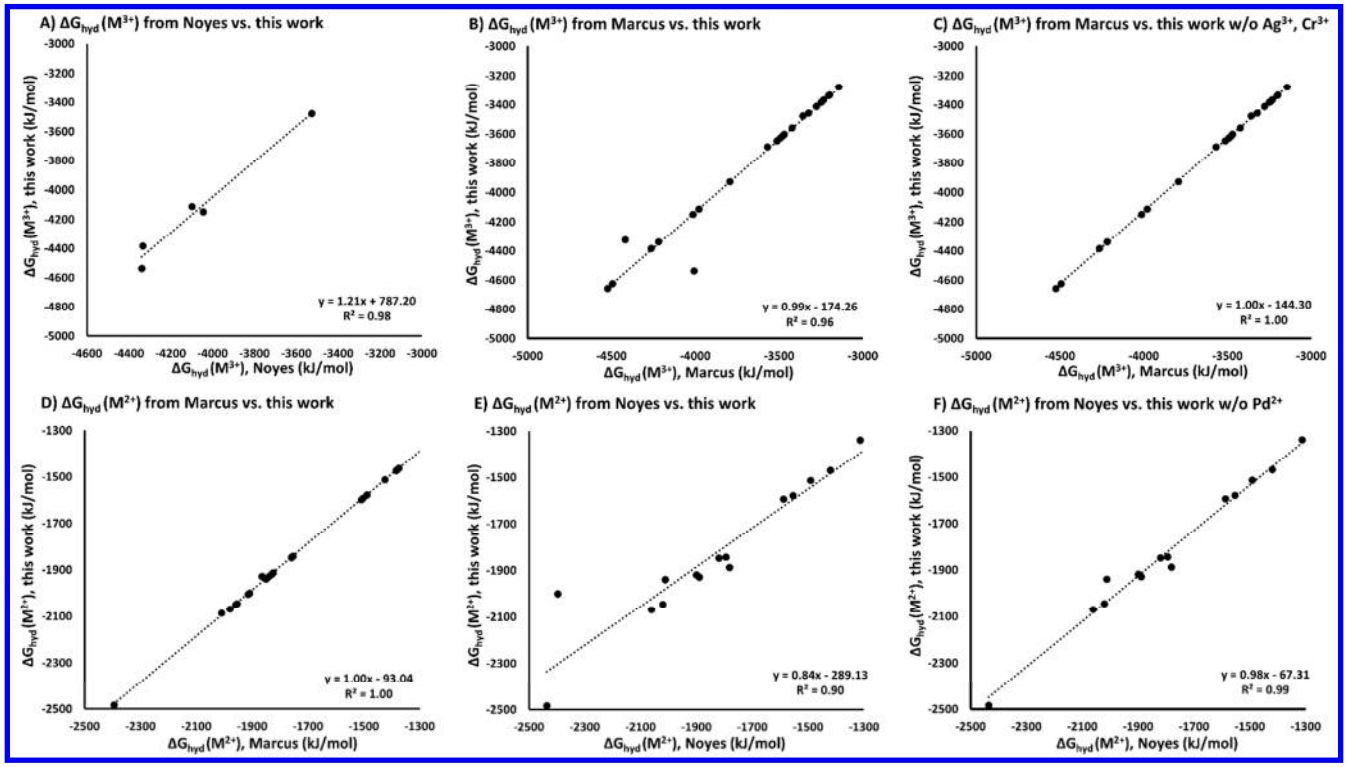

Figure 3. A) Comparison of free energies of hydration for M^{3+} ions from this work with those reported by Noyes. **B)** Same compared with values reported by Marcus. **C)** Same but with the values for Cr^{3+} and Ag^{3+} removed from the comparison. **D)** Comparison of free energies of hydration for M^{2+} ions from this work with those reported by Marcus. **E)** Same compared with values reported by Noyes. **F)** Same, but with the value for Pd^{2+} removed from the comparison.

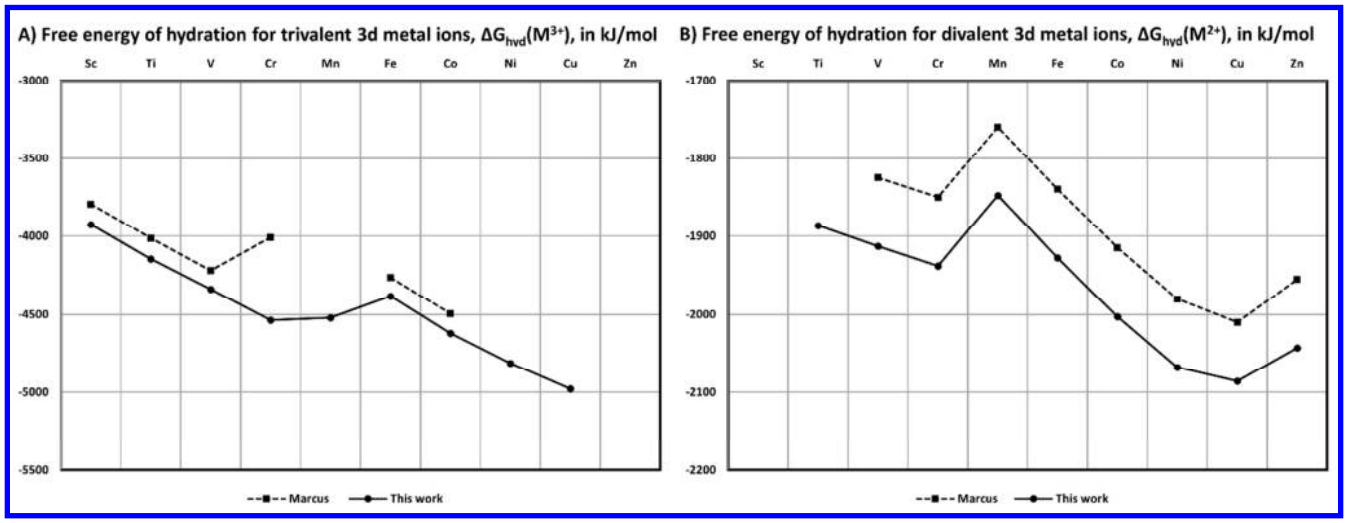

Figure 4. A) Free energy of hydration for 3d M^{3+} ions from this work and from Marcus. **B)** Free energy of hydration for 3d M^{2+} ions from this work and from Marcus[10,11].

We now discuss some chemical implications of the ΔG_{hyd} values not reported before. Of particular interest is the trend in the behavior of ΔG_{hyd} for the same oxidation state across the d transition series. **Figure 4** shows the values of ΔG_{hyd} from this work and from the compilation by Marcus for the 3d M^{3+} (**Figure 4A**) and M^{2+} ions (**Figure 4B**). The entropy of hydration, ΔS_{hyd}, is similar for the ions of the same charge due to their similar overall effect on bulk water structure[11]. Thus, the free energies are expected to follow closely the trend for ΔH_{hyd}.

For the 3d M^{3+} ions seen in **Figure 4A**, five values were compiled by Marcus. Based on the thermochemical cycle calculations, a total of nine of the ten ΔG_{hyd} values are now available on a consistent scale (the value for Zn^{3+} remains elusive due to the instability of this redox state). As expected, ΔG_{hyd} becomes more negative toward the right of the 3d transition series as the increased effective nuclear charge makes the lone pairs of water molecules associate more strongly with the metal ions. In addition, deviations from linearity result from the effect of the occupation of e_g vs. t_{2g} orbitals, which also translates into the ligand field stabilization energy. Occupation of e_g orbitals lowers the ligand field stabilization energy and reduces the association with water lone pairs due to the increased repulsion with d-electrons in the e_g orbitals that point directly towards the water lone pairs. These two effects are well-known and described in text books for $\Delta H_{hyd}(M^{2+})$[35], but not previously for M^{3+}. The notable difference between the two series is the difference in one d-electron, which leads the bump to be at Cr^{3+} rather than at V^{2+}; both being d^3 systems with maximal ligand field stabilization energy for the first half of the series.

The $\Delta G_{hyd}(Cr^{3+})$ value reported by Marcus can now be seen to be inconsistent with these trends, whereas the new value derived here (**Table 1**) is fully consistent with the expected physical effect of the ligand field. For the same reason, the new value for Mn^{3+} (−4520 kJ/mol) is excellently on the expected trend, having a smaller ligand field stabilization energy (d^4) but a higher effective nuclear charge making its value only slightly higher than that of Cr^{3+}. Mn^{3+} has, as far as the author is aware, not been reported before probably due to the instability of the species in solution. $\Delta G_{hyd}(Fe^{3+})$ forms a local maximum in the trend directly explained from its zero ligand field stabilization energy, whereas subsequent metal ions, notably the new consistent values for Ni^{3+} and Cu^{3+}, monotonously increase their ligand field stabilization energy to make hydration more favorable. From the new established trend in **Figure 4A**, one can estimate that ΔG_{hyd} of the experimentally elusive Zn^{3+} is smaller than −4900 kJ/mol on the scale applied here; this ion has so far never been observed and is possibly only of

theoretical interest. If one considers its likely Jahn-Teller distortion, $\Delta G_{hyd}(Zn^{3+})$ will most likely be between −5000 and −5100 kJ/mol; this value could probably be estimated theoretically.

In terms of $\Delta G_{hyd}(M^{2+})$, a consistent series (**Figure 4B**) is now available for the entire 3d transition series except Sc^{2+}, with the value for Ti^{2+} derived from the thermochemical cycle being excellently on the expected trend. The overall trend in $\Delta G_{hyd}(M^{2+})$ is essentially identical to the known trend in $\Delta H_{hyd}(M^{2+})$[35] due to the similar hydration entropy of the species, and follows from the same arguments as applied above. More generally, the excellent trends in **Figure 4** show that trend properties of hydrated metal ions derive mainly from electronic structure effects of the first hydration sphere, with additional water having a relatively similar constant contribution.

Using similar considerations, we can now also resolve the conflicting data on $\Delta G_{hyd}(Pd^{2+})$. Simple interpolation from Ag^{2+} (−1928 kJ/mol) and Cd^{2+} (−1843 kJ/mol) gives a linear trend with the value −1998 kJ/mol, which fits well to the loss of ligand field stabilization energy toward the far right of the 4d transition series, as also seen for the Ni^{2+}/Zn^{2+} comparison, and with energies similar to those of the 3d transition series. This strongly argues against the alternative value -2397 kJ/mol, which is far outside the range expected for the series as a whole and is not physically meaningful from a trend comparison viz. the above discussion. The trend using -1998 kJ/mol also interestingly predicts that the strong Jahn-Teller distortion that produces the anomalously negative $\Delta G_{hyd}(Cu^{2+})$ is essentially absent in Ag^{2+}, although this remains to be confirmed experimentally.

CONCLUSION

In summary, this paper has used the conventions on the SHE and free energy of hydration of the proton and a thermochemical cycle that relies on cancellation of the difficult metal states, to derive free energies of hydration in **Table 1** and **2** that are all consistent with each other within the thermochemical cycle, as they should be. The use of trend comparisons enables the major revision of some previous values, notably for Au^{3+}, Cr^{3+}, and $Pd^{2+,}$ and reveals the first complete trend for the hydration from Sc^{3+} to Cu^{3+} which is physically meaningful and well explained by the combination of effective nuclear charge and e_g orbital occupation effects. Entirely new values have been obtained for many ions such as Ag^{3+}, Cu^{3+}, Mn^{3+}, Ni^{3+}, Au^{2+}, and lanthanide M^{2+} states, some of which are very hard to produce experimentally whereas others should not be. The new values should hopefully be of

use in other thermochemical calculations, for interpreting the aqueous behavior of the involved metal ions, and as benchmarks for theoretical chemistry.

SUPPORTING INFORMATION

The Supporting Information file contains Table S1 with experimental standard half reduction potentials (in V) and first, second, and third ionization potentials (in eV) used for the calculations done in this work. This file is available free of charge at http://pubs.acs.org

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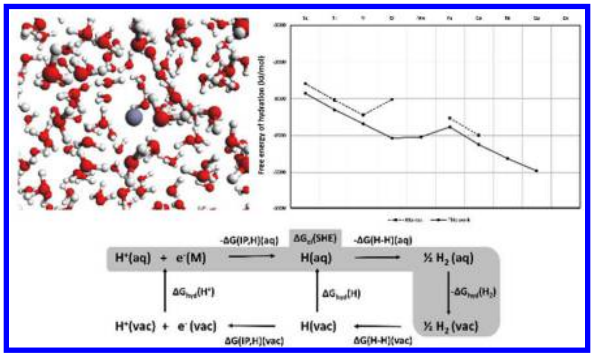
TOC graphic



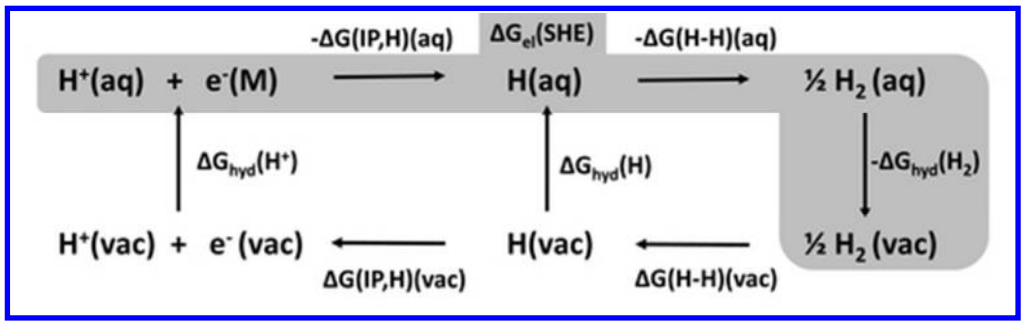


Figure 1

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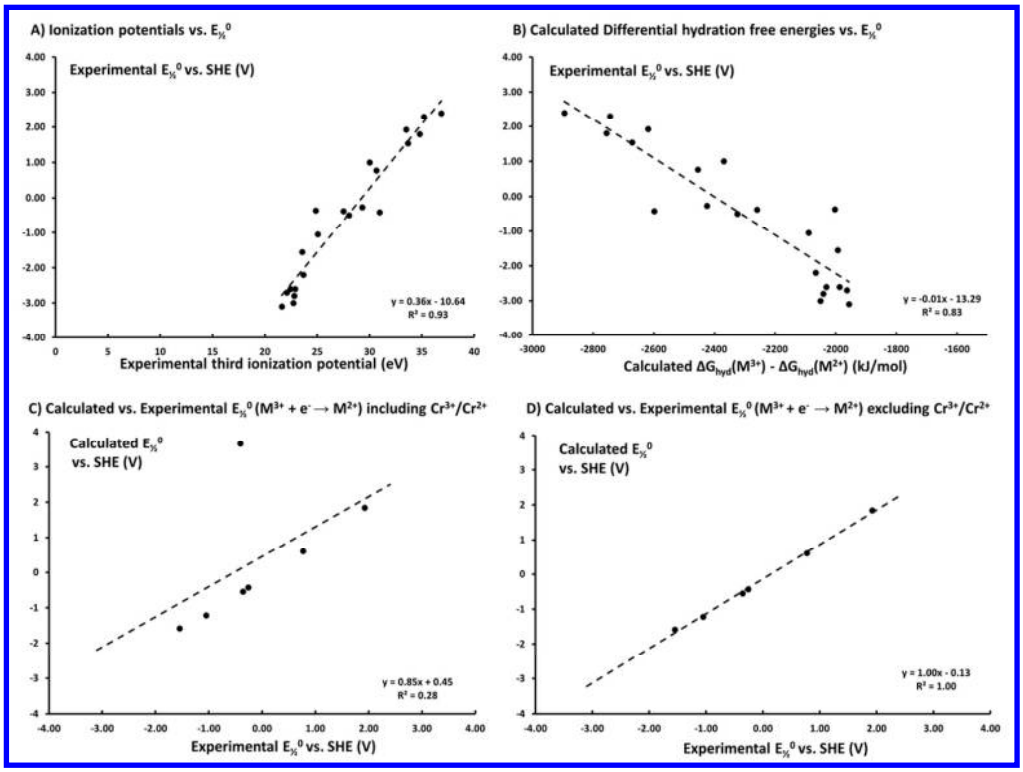

Figure 2

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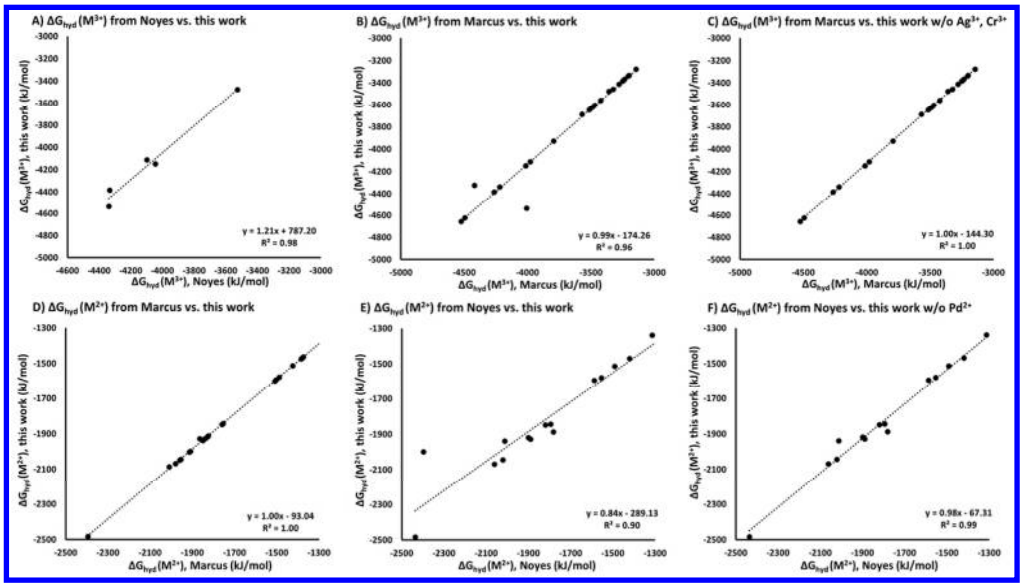

Figure 3

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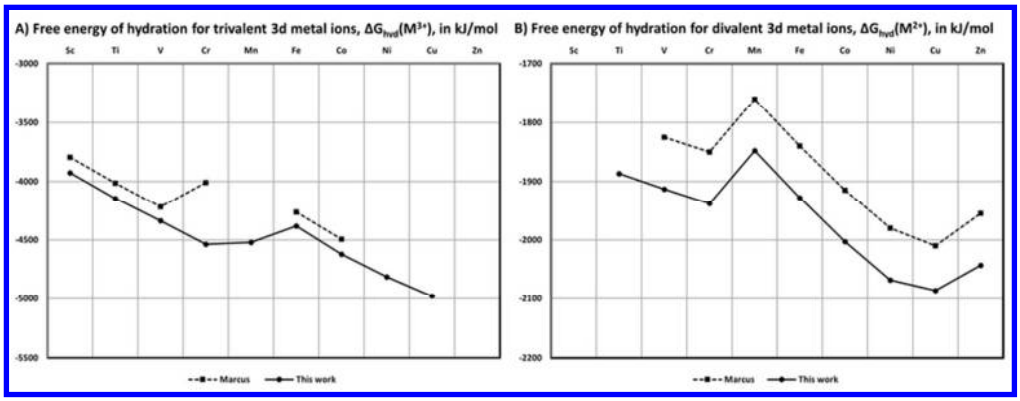

Figure 4

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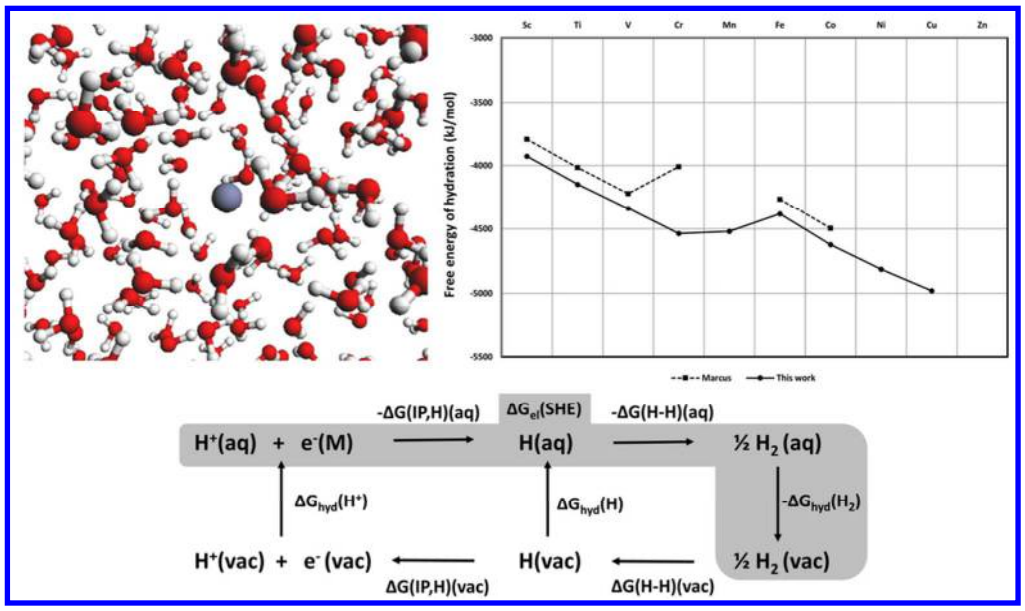

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